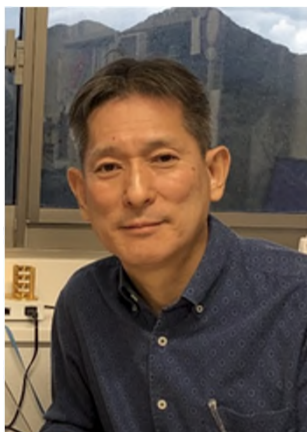


# CBC Virtual Seminar Series



**Professor Ken Sakai**  
Kyushu University, Japan

## Catalysis of Transition Metal Complexes in Water Splitting and CO<sub>2</sub> Reduction: Improved Understanding in the Reaction Pathways

Since the initial discovery in 1987 (J. Coord. Chem. 1988, 18, 169) in the catalytic activity of platinum(II) compounds in hydrogen evolution reaction (HER), continued efforts have been made to gain deeper understanding in the mechanism of molecular catalysis by various transition metal compounds in some important energy related catalytic reactions such as HER, OER (oxygen evolution reaction), and carbon dioxide reduction (CDR). For the reduction side of catalysis (HER and CDR), the manner how we utilize/tune either the electron density or basicity at the filled d orbital exposed at the reaction center plays a key role in promoting the protonation or CO<sub>2</sub>-binding step which is often the rate-determining steps (RDSs). In such RDSs (i.e.,  $M(d^8) + H^+ \rightarrow M(d^6)(H)^+$  or  $M(d^8) + CO_2 \rightarrow M(d_6)(CO_2^{2-})$ ), the filled  $d_{z^2}$  orbital in a square-planar or distorted square pyramidal  $d^8$  metal ion is generally required with a limited number of exceptions, which has become increasingly clearer based on our recent Experimental/DFT hybrid studies. The  $d^8$  Pt(II), Ni(II), Co(I), and Rh(I) are good candidates due to their easily accessible characters under ambient or weakly reducing conditions. However, these systems often require further reduction at the metal-ligand or ligand orbitals that are closely located to the reactive metal center, in part due to the lack of driving force to promote the HER or CDR. On the other hand, Fe(0) and Mn(-I) are also known to be useful candidates only when they are coordinated by strongly  $\pi$ -back bonding ligands such as carbon monoxide (CO), as demonstrated by the naturally evolved [FeFe]-hydrogenase enzyme and Mn(bpy)(CO)<sub>3</sub>Br. However, with the lack of CO-like ligands stabilizing such low valent systems, Fe(0) requires relatively strongly reducing conditions and thereby exhibits slow catalysis when driven by the standard photosensitizers like Ru(bpy)<sub>3</sub><sup>2+</sup> or organic dyes due to the insufficient driving forces available for the reactive intermediate formation step. **(refer to next page for full abstract)**

### Biography

Ken Sakai grew up in a country side of Japan (Misasa) where he largely enjoyed playing in nature, like catching fish, mountain hiking, and camping. He received his B.S. (1987), M.S. (1989), and Ph.D. (1993) at Waseda University in Tokyo, and became an assistant professor at Seikei University in 1991, an associate professor at Tokyo University of Science in 1999, and then a full professor at Kyushu University in 2004. His interests involve studies leading to improved understanding of various important catalytic reactions together with the development of hybrid materials serving as artificial photosynthetic nano-photoreactors for solar fuel generation.

**Date:** 19<sup>th</sup> June 2020, Friday  
**Time:** 1.00 pm to 2.30 pm  
**Venue:** Zoom Platform  
**Host:** Associate Professor Soo Han Sen

**For Zoom registration:**



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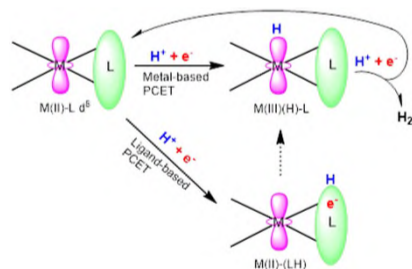
### Catalysis of Transition Metal Complexes in Water Splitting and CO<sub>2</sub> Reduction: Improved Understanding in the Reaction Pathways

#### Full Abstract

Since the initial discovery in 1987 (J. Coord. Chem. 1988, 18, 169) in the catalytic activity of platinum(II) compounds in hydrogen evolution reaction (HER), continued efforts have been made to gain deeper understanding in the mechanism of molecular catalysis by various transition metal compounds in some important energy related catalytic reactions such as HER, OER (oxygen evolution reaction), and carbon dioxide reduction (CDR). For the reduction side of catalysis (HER and CDR), the manner how we utilize/tune either the electron density or basicity at the filled d orbital exposed at the reaction center plays a key role in promoting the protonation or CO<sub>2</sub>-binding step which is often the rate-determining steps (RDSs). In such RDSs (i.e.,  $M(d^8) + H^+ \rightarrow M(d^6)(H)^+$  or  $M(d^8) + CO_2 \rightarrow M(d^6)(CO_2^{2-})$ ), the filled  $d_{z^2}$  orbital in a square-planar or distorted square pyramidal  $d^8$  metal ion is generally required with a limited number of exceptions, which has become increasingly clearer based on our recent Experimental/DFT hybrid studies. The  $d^8$  Pt(II), Ni(II), Co(I), and Rh(I) are good candidates due to their easily accessible characters under ambient or weakly reducing conditions. However, these systems often require further reduction at the metal-ligand or ligand orbitals that are closely located to the reactive metal center, in part due to the lack of driving force to promote the HER or CDR. On the other hand, Fe(0) and Mn(-I) are also known to be useful candidates only when they are coordinated by strongly  $\pi$ -back bonding ligands such as carbon monoxide (CO), as demonstrated by the naturally evolved [FeFe]-hydrogenase enzyme and Mn(bpy)(CO)<sub>3</sub>Br. However, with the lack of CO-like ligands stabilizing such low valent systems, Fe(0) requires relatively strongly reducing conditions and thereby exhibits slow catalysis when driven by the standard photosensitizers like Ru(bpy)<sub>3</sub><sup>2+</sup> or organic dyes due to the insufficient driving forces available for the reactive intermediate formation steps.

The RDSs are often classified into metal- and ligand-based proton-coupled electron transfer (PCET) for HER and OER, while the RDSs for CDR may be those coupled to CO<sub>2</sub>-binding step instead of either protonation or deprotonation. Our recent study on the Co-NHC catalysts clearly indicates that the strongly donating NHC permits the catalyst to take the metal-centered PCET pathway to evolve a hydride intermediate, which has also been supported by our DFT results. The CO<sub>2</sub> binding to Co(I)(porphyrin-•) rather than Co(I)(porphyrin) is largely favored due to the higher electron density at the metal center due to the additional negative charge dispersed over the porphyrin. The hydride formation in the Pt(II)-catalyzed HER undergoes via formation of a metal-metal  $d_{z^2}$ - $d_{z^2}$  association in a stacked dimer in solution to accelerate the RDS yielding a hydridodiplatinum(II,III) intermediate;  $Pt(II)_2 + H^+ + e^- \rightarrow Pt(II)Pt(III)(H)$ . One of our recent finding involves the quartet  $d^7$  Fe(I) species which triggers the CO<sub>2</sub> binding using two d- $\pi$  orbitals, where one is a filled orbital and the other is a half filled (singly occupied MO). These systems will be discussed. The reaction obeys a scheme of  $M(d^7) + CO_2 \rightarrow M(d^5)(CO_2^{2-})$  in quartet states.

As for the OER, due to the wide range of higher valence oxidation levels available for Mn, Fe, and Ru, they are known to effectively catalyze OER by mainly relying on the metal-centered redox processes in affording the electron deficient Oxygen center required to promote the O-O coupling considered as the RDS. They can utilize  $d^4$  Mn(III),  $d^3$  Mn(IV),  $d^2$  Mn(V),  $d^4$  Fe(IV)+Ru(IV), and  $d^3$  Fe(V)+Ru(V) in order to enhance deprotonation of the aqua ligand bound to the metal ion without using any ligand-based hole charging processes. In contrast with these metals with lower nuclear charge due to lower atomic numbers, the single-site Co or Cu porphyrins or phthalocyanines, adopted in our recent studies, can only make access to  $d^5$  Co(IV) and  $d^8$  Cu(III), respectively, as the highest metal oxidation levels. However, these levels are not purely metal-based and must be defined as 'formal Co(IV) and Cu(III), respectively'. Therefore, these must largely rely on the hole-charging at the porphyrins and phthalocyanines. Our recent DFT provides an intriguing and attractive features of the mechanism of OER taken by the Co porphyrins. Part of these studies will also be discussed.



#### Relevant Publications:

- 1"Photochemical CO<sub>2</sub> Reduction Driven by Water-Soluble Copper(I) Photosensitizer with the Catalysis Accelerated by Multi-Electron Chargeable Cobalt Porphyrin", Xian Zhang, Mihaela Cibian, Arnau Call, Kosei Yamauchi, and Ken Sakai, ACS Catal. 2019, 9, 11263-11273.
- 2"An Earth-abundant System for Light-driven CO<sub>2</sub> Reduction to CO Using a Pyridinophane Iron Catalyst", Yuto Sakaguchi, Arnau Call, Mihaela Cibian, Kosei Yamauchi and Ken Sakai, Chem. Commun. 2019, 55, 8552-8555.
- 3"A Molecular Cobalt Hydrogen Evolution Catalyst Showing High Activity and Outstanding Tolerance to CO and O<sub>2</sub>", Jia-Wei Wang, Kosei Yamauchi, Hai-Hua Huang, Jia-Kai Sun, Zhi-Mei Luo, Di-Chang Zhong, Tong-Bu Lu, and Ken Sakai, Angew. Chem. Int. Ed. 2019, 58, 10923-10927.
- 4"Mechanisms of Water Oxidation using Ruthenium, Cobalt, Copper, and Iron Molecular Catalysts", Alexander Rene Parent, Takashi Nakazono, Yuta Tsubonouchi, Natsuki Taira and Ken Sakai, Adv. Inorg. Chem. 2019, 74, 197-240.
- 5"Highly Efficient and Selective Photocatalytic CO<sub>2</sub> Reduction to CO in Water by a Cobalt Porphyrin Molecular Catalyst", Arnau Call, Mihaela Cibian, Keiya Yamamoto, Takashi Nakazono, Kosei Yamauchi, and Ken Sakai, ACS Catal. 2019, 9, 4867-4874.
- 6"Ligand-based PCET Reduction in a Heteroleptic Ni(bpy)(dithiolene) Electrocatalyst Giving Rise to Higher Metal Basicity Required for Hydrogen Evolution", Keita Koshiba, Kosei Yamauchi, and Ken Sakai, ChemElectroChem 2019, 6, 2273-2281.
- 7"Consecutive Ligand-based PCET Processes Affording a Doubly Reduced Nickel Pyrazinedithiolate which Transforms into a Metal Hydride Required to Evolve H<sub>2</sub>", Keita Koshiba, Kosei Yamauchi, and Ken Sakai, Dalton Trans. 2019, 48, 635-640.
- 8"A family of molecular nickel hydrogen evolution catalysts providing tunable overpotentials using ligand-centered proton-coupled electron transfer paths", Yutaro Aimoto, Keita Koshiba, Kosei Yamauchi and Ken Sakai, Chem. Commun. 2018, 54, 12820-12823.
- 9"A Nickel Dithiolate Water Reduction Catalyst Providing Ligand-based Proton-coupled Electron Transfer Pathways", Keita Koshiba, Kosei Yamauchi, and Ken Sakai, Angew. Chem. Int. Ed. 2017, 56, 4247-4251.
- 10"Improving the robustness of cobalt porphyrin water oxidation catalysts by chlorination of aryl groups", Takashi Nakazono and Ken Sakai, Dalton Trans. 2016, 45, 12649-12652.
- 11"Photochemical Water Oxidation Catalysed by a Water-Soluble Copper Phthalocyanine", Ryota Terao, Takashi Nakazono, Alexander Rene Parent, and Ken Sakai, ChemPlusChem 2016, 81, 1064-1067.
- 12"Improved Photocatalytic Hydrogen Evolution Driven by Chloro(terpyridine)platinum(II) Derivatives Tethered to a Single Pendant Viologen Acceptor", Shu Lin, Kyoji Kitamoto, Hironobu Ozawa, and Ken Sakai, Dalton Trans. 2016, 45, 10643-10654.
- 13"Photochemical H<sub>2</sub> Evolution from Water Catalyzed by Dichloro(diphenylbipyridine)platinum(II) Derivative Tethered to Multiple Viologen Acceptors", Kyoji Kitamoto and Ken Sakai, Chem. Commun. 2016, 52, 1385-1388.
- 14"Improving Singlet Oxygen Resistance during Photochemical Water Oxidation by Cobalt Porphyrin Catalysts", Takashi Nakazono, Alexander Rene Parent and Ken Sakai, Chem. Eur. J. 2015, 21, 6723-6726.
- 15"Progress in Base-Metal Water Oxidation Catalysis", Alexander Rene Parent and Ken Sakai, ChemSusChem 2014, 7, 2070-2080.
- 16"A Cobalt-NHC Complex as an Improved Catalyst for Photochemical Hydrogen Evolution from Water", Ken Kawano, Kosei Yamauchi and Ken Sakai, Chem. Commun. 2014, 50, 9872-9875.
- 17"Cobalt Porphyrins as Homogeneous Catalysts for Water Oxidation", Takashi Nakazono, Alexander Rene Parent, and Ken Sakai, Chem. Commun. 2013, 49, 6325-6327.